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Measurement of Volatile Organic Compounds

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Measurement of Volatile Organic Compounds

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16. ABSTRACT

This document discusses the rationale of total volatile organics stationary source emission measurement through the determination of organic carbon mass concentration. A conceptual approach for writing emission regulations in terms of volatile organic carbon is recommended, and drafts of two specific test methods are presented for regulation implementation. The methods are the measurement of total gaseous nonmethane organics as carbon by the chromatographic oxidation/reduction procedure, and the relative organic measurement derived by direct application of the flame ionization analyzer.

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Emissions Measurement Branch
Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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PREFACE

Emphasis on the control of volatile organic compounds through the State Implementation Plans, new source performance standards, and national emission standards for hazardous air pollutants has created a need for standardized test procedures. In setting national performance standards for new sources and national emission standards for hazardous air pollutants, the Environmental Protection Agency has followed a policy of establishing a reference method for each regulated source category and pollutant. Under the State Implementation Plan process, however, test methods and procedures are defined by the States. Thus, the case-by-case approach used by the Environmental Protection Agency for national standards could conflict with State established methods. In addition, the case-by-case approach does not provide sufficient guidance to the States in their efforts to develop regulations for a large number of sources and organic compounds.

The purpose of this document, therefore, is to provide guidance to the States on the measurement of volatile organic compounds from a diversity of sources and pollutants that is consistent with the methodology being applied by the Environmental Protection Agency as it develops regulations for specific sources and pollutants.

Significant revisions to this document consist of refinements to the measurement procedure described in "Attachment 2."

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METHODS FOR DETERMINING VOLATILE ORGANIC COMPOUNDS AS CARBON IN STATIONARY SOURCES

Introduction

Volatile organic compound (VOC) emission control regulations are being developed by EPA and by State and local agencies to meet the oxidant control needs. In some cases, the regulations are in terms of the volatile organic content of solvents. In other cases, they cover organic volume or mass concentrations, mass emission rates, and control equipment efficiencies. Regardless of the approach taken in the regulation, consideration must be given to the expression of emission limits in terms of what can be measured, and to the cost and practicality of the test methods.

One concept of volatile organic emission measurement is the determination of organic carbon mass concentration. The rationale for selecting this concept and conceptual approach for writing regulations in terms of volatile organic carbon are discussed herein, and two specific test methods are presented to implement the recommended approach.

Rationale for Selecting Organic Carbon

In considering volatile organic compound test methods one must recognize that organic emissions normally consist of a mixture of compounds and that there is presently no detection technique having an inherent, quantitative response to the total molecular structure of the mixture. Several detection techniques respond to organic compounds; however, the response can vary widely from compound to compound and may, therefore, not be proportional to the total organic mass or volume in a mixture.

Such is the case of the flame ionization detector (FID), the most commonly used detector for organic measurements. The FID response can vary from compound to compound because it is a function of the number of carbon atoms, the type of bonds, and the elements present in the organic molecules. Thus, if the volatile organic emission limit is expressed in terms that require the measurement of the total molecular structure of the organic emissions, the variable response of the flame ionization detector must be overcome by one of the methods described below.

1. Gas Chromatograph/Flame Ionization Detector. This method involves the separation of the organic components into discrete compounds using gas chromatography (GC). The compounds are identified, and the FID is calibrated for each of the identified compounds. The compounds are then measured individually, and the total mass concentration is determined by adding the individual mass concentration values; methane can be identified and excluded from the results. This method may be practical where only two or three compounds are emitted, such as in maleic anhydride plants; but if it is applied to sources that emit numerous organics, the time and expense would be formidable. For example, over 20 peaks were noted in a preliminary study of emissions from the manufacture of nitrobenzene.

2. Direct Flame Ionization Detector with Emission Stream Characterization. This method involves direct measurement with an FID analyzer,

with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic components in the stream. If present, methane will, of course, also be measured.

In practice, this method can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under the following limited conditions: (1) where only one compound is known to exist, (2) when the organic compounds consist of only hydrogen and carbon, (3) where the relative percentage of the compounds is known or can be determined, and the FID response to the compounds is known; (4) where a consistent mixture of compounds exists before and after emission control and only the relative concentrations are to be assessed, or (5) where the FID can be calibrated against mass standards of the emissions (solvent emissions, for example).

In the case of volatile organic solvents, accurate measurements by direct FID analyzers without calibration with solvent standards are seldom possible because these solvents are often a mixture of multiple unknown compounds. Even if the emissions can be separated and identified using a GC, accurate determination of the average FID response is often impractical. In addition, the emissions may be altered as they pass through a control device: for example, they may be partially oxidized in an incinerator or selectively retained in an adsorber. In such cases the measurement is more difficult and cannot be corrected with

solvent standards; therefore even the determination of percent control efficiency can be a difficult problem.

Another applicable measurement technique involves an oxidation-reduction analysis; however, the results of this technique are in terms of organic carbon and not a mass concentration of the total molecular structure. In this approach, the nonmethane organic compounds are separated from other carbon compounds and are then oxidized to CO_2. The resultant CO_2 is subsequently reduced to methane, which is then measured with an FID. The CO_2 from the combustion step can also be measured with a nondispersive infrared (NDIR) analyzer; however, the NDIR is not as sensitive as the FID and is therefore limited to high concentration levels. One limitation to the oxidation-reduction analysis is that the equipment required is somewhat complex and is unlikely to be made available in a portable form.

Consideration of the various measurement approaches indicates that organic emission regulations expressed in terms of the measurement of organic carbon could be applied to a wide range of volatile compounds. The measurement of organic carbon can be used to assess directly the efficiency of control devices such as incinerators or adsorbers. By performing volumetric flow rate measurements, one can then determine organic carbon emission rates. Organic carbon content can also be related to volatile

content of solvents or surface coatings.

Costs, logistics, and other practicalities of source testing may, under limited conditions, make other test methods more desirable for routine compliance determinations. Three distinct categories of test methods are therefore recommended for use with volatile organic compound regulations expressed in terms of organic carbon: a reference method, alternate methods, and screening methods. These categories are described as follows:

1. Reference Method. This method would be applicable to all regulated sources and would be accurate in reference to the emission standard. OAQPS recommends that the reference method be based on the oxidation-reduction method of analysis to measure organic carbon.
2. Alternate Methods. These are methods not necessarily demonstrated to be equivalent to the reference method, but demonstrated to the satisfaction of the control agency to produce results adequate for determining compliance, in specific applications. Methods involving direct measurement with flame ionization detectors would be primary candidates for alternate methods.
3. Screening Methods. These alternative methods may produce biased or imprecise results, but they have been demonstrated to the satisfaction of the control agency to be adequate for determining compliance, provided that any bias or imprecision is taken into account. These

methods are normally characterized by portability of equipment, procedural simplicity, and low cost. Methods based on thermal conductivity or low-cost portable FID analyzers would be candidates for approval as screening methods.

Recommended Reference Method

A reference method that involves indirect measurement of volatile organic carbon by an oxidation-reduction is recommended. This necessitates that the emission limits be expressed in terms of organic carbon. If the emission limits and a universal reference method are both based on organic carbon, the volatile organic standard will be expressed in clear, unambiguous terms. No other known practical test method could accomplish this objective for a wide range of volatile organic compounds.

A draft "Reference Method for Determination of Total Gaseous Nonmethane Organic Emissions as Carbon" is included as Attachment 1. The method requires a system for separating total nonmethane organics from other carbon compounds, converting the total nonmethane organics to methane, and analysis of the methane by a flame ionization detector. Other than requiring this general equipment, the method provides performance specifications designed to assure correct performance of the separation-detection system. Depending on the organic carbon concentration, the method may allow the use of the NDIR to detect the CO_2 formed by the initial oxidation step.

The concept upon which the method is based has been utilized for many years in Los Angeles County, where it has been demonstrated to be valid and effective for compliance determinations.

There is at least one private laboratory that is able to perform the analysis on a fee basis. The oxidation-reduction analysis concept for measurement of gaseous nonmethane organic compounds is also offered commercially by at least one instrument vendor. Although the availability of instruments is admittedly very limited, there is no serious technical impediment that would prevent additional vendors from designing and producing acceptable instruments.

Because of the somewhat limited use potential for the Los Angeles laboratory-oriented procedure and the present limited production of commerical instruments for field use, the OAQPS recommendation of the oxidation-reduction reference method for the definition of organic emissions is recognized as leading the technology. Wide acceptance of the organic carbon reference method will, however, provide the needed inducement for additional vendors to enter the market and thereby increase the supply and variety of organic carbon analysis instruments.

A draft of the Los Angeles procedure is included as Attachment 2. Although the detail is considerable, some agencies may wish to assemble the laboratory apparatus. The Emission Measurement Branch of OAQPS is working to refine the operating details of the procedure; as information becomes available, it will be incorporated into the method.

Alternate Methods

An "Alternate method" may have only limited applicability or other deficiencies that prevent its designation as a reference method. Such methods may offer practical advantages and produce results adequate for determining compliance in certain applications. Where such methods are applicable, the results may be accepted in lieu of reference method results.

As a specific example, methods based on direct measurement with flame ionization detectors are often practical for hydrocarbon compounds, and, in addition, the equipment is widely available. An FID analyzer will be less costly and may be less complicated for field application that an oxidation-reduction analyzer; therefore, for those applications where such methods can be made to produce accurate results, approval of them as alternate methods is desirable.

The Office of Air Quality Planning and Standards, EPA,has drafted an "Alternate Test Method for Direct Measurement of Total Gaseous Organic Compounds Using a Flame Ionization Detector," which is included as Attachment 3. This method outlines the known characteristics and limitations of FID techniques and provides procedures needed to assure its proper operation. The method does not and is not intended to indicate specific applications where the method can (or cannot) be used or correction factors to be applied to the results. Such determinations must be made on a case-by-case basis founded on knowledge of

the contents of the stream under test and the limitations of the detector.

Screening Methods

In addition to the limitations associated with alternate methods, screening methods may also lack precision. In spite of such shortcomings, screening methods may play an important role in any volatile organic control program. As a practical matter, the cost of applying a reference or alternate method to all or even a majority of the regulated effluent streams in a jurisdiction may be unreasonable; therefore, less expensive, simpler testing techniques will be needed.

To date, OAQPS has made effective use of an explosimeter to detect vapor leaks in gasoline marketing operations. More recently, OAQPS has initiated a test program associated with the development of new source standards, using portable analyzers to detect leaks occurring in unit operations in the petroleum industry. Two analyzers will be employed in this program, one involving a combustion/thermal-conductivity-type detector and the other a portable FID.

Another example of a screening method would be the case of an FID analyzer applied to an unknown gas stream. In such case there is often enough information available to provide a rough estimate of the analyzer accuracy, but a more exact determination would be prohibitive. In such an event the FID

may be used as an alternative method for determining compliance, provided that sufficient buffer is included to account for the possible inaccuracy.

Regulatory Language

Examples of how general regulations may be expressed in terms of the reference method that measures organic carbon concentration are as follows:

1. To regulate concentration:

   "Emissions of organic carbon shall not exceed_____ grams carbon per cubic meter."

2. To regulate mass rate:

   "Emissions of organic carbon shall not exceed_____ grams carbon per hour" or "Emissions of organic carbon shall not exceed_____ grams carbon per kilogram of solvent used."

To protect the analytical instrument from contamination from particulates, and to prevent loss of volatile organics due to condensation, a filter and heated sample line (both temperature defined) must also be specified in the emission regulations.

ATTACHMENT 1. REFERENCE METHOD FOR DETERMINATION OF TOTAL GASEOUS NONMETHANE ORGANIC EMISSIONS AS CARBON--AUTOMATED ANALYZER VERSION

1. Principle and Applicability

1.1 Principle. Conditioned stack gas is transported to and analyzed by a semiportable gas chromatograph (GC) equipped with a flame ionization detector (FID). The total gaseous nonmethane organic (TGNMO) fraction is separated by means of various GC columns from the other constituents, oxidized to CO_2 and then reduced to methane (CH_4) before it is introduced to the FID. In this manner, the variable response of the FID associated with different types of organics is eliminated, and a count of TGNMO carbon atoms is obtained.

1.2 Applicability. The method is applicable to the semicontinuous measurement of total gaseous nonmethane organics in source emissions.

2. Range and Sensitivity

2.1 Range. Signal attenuators shall be available so that a minimum signal response of 10 percent of full scale can be produced when analyzing calibration gas or sample.

2.2 Sensitivity. The detector sensitivity shall be equal to or better than 2.0 percent of the full scale setting, with a minimum full scale setting of 10 ppm (methane or carbon equivalent).

3. Interferences

None.

4. Apparatus

4.1 TGNMO analyzers are available commercially or can be constructed from available components by a qualified instrument laboratory. The

primary components of the analyzer are an FID preceded by a GC column to achieve the necessary separation of TGNMO from other carbon compounds. Oxidation and reduction catalysts then convert the TGNMO to CH_4 prior to detection. The analyzer shall be accompanied by an instruction manual (supplied by the manufacturer if the analyzer was commercially produced) describing proper operation and maintenance procedures. In addition to the specific procedures required by this method, the analyzer shall be demonstrated prior to initial use to be capable of proper separation, oxidation, and reduction. As a minimum this demonstration shall include measurement of a known TGNMO concentration present in a mixture that also contains similar amounts of CH_4, CO_2, and CO. Certification of such demonstration by the manufacturer is acceptable.

4.2 Sample Conditioning or Interface System (see Figure 1). Probe with filter, 6.4 mm O.D. Teflon[1] sample line, Teflon-coated diaphragm pump, and Teflon flow control valves. A heating system capable of maintaining all components at 120°C or greater shall be included. The pump shall be sized so that the sample residence time from the probe to the instrument will not exceed 15 seconds.

4.3 Potentiometric Recorder (optional). Strip chart recorder with a voltage output compatible with the analyzer.

5. Reagents

5.1 Combustion Gas. Air containing less than 2 ppm organics (methane or carbon equivalent).

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[1]Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

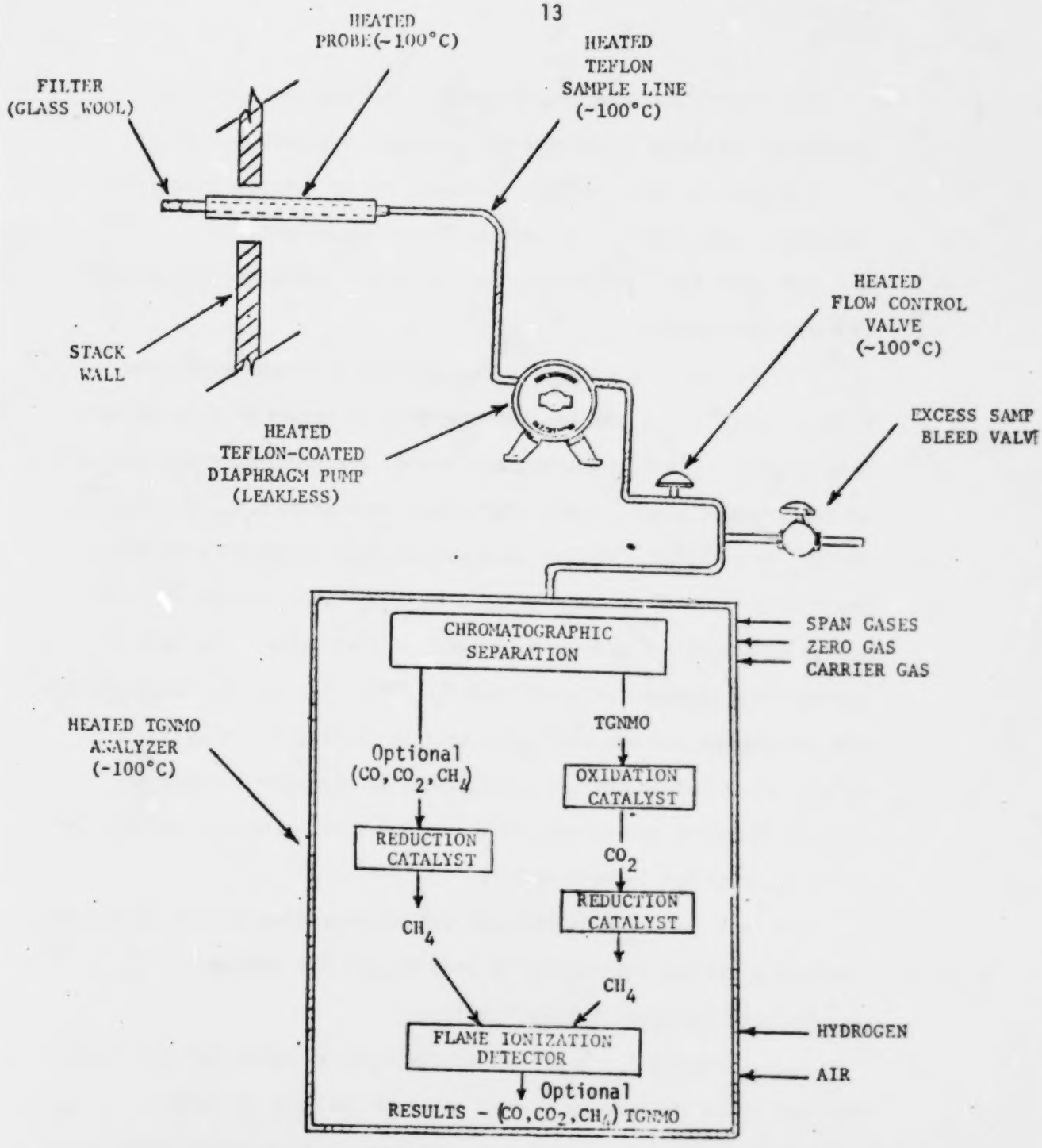

FIGURE 1. On-site Application of TGNMO Analyzer

5.2 Fuel. Hydrogen or a mixture of hydrogen and inert gas containing less than 1 ppm organics (methane or carbon equivalent).

5.3 Carrier Gas. Helium, nitrogen, air or hydrogen containing less than 1 ppm organics (methane or carbon equivalent).

5.4 Zero Gas. Air containing less than 1 ppm organics (methane or carbon equivalent).

5.5 Calibration Gases (2). Gas mixture standards with known propane (C_3H_8) concentrations corresponding to ranges of 5-10 ppm and 5-10 percent (methane or carbon equivalent) are prepared and certified by a gas manufacturer. The mixture shall consist of C_3H_8, CO, CO_2, and CH_4 in nitrogen. The gas manufacturer must recommend a maximum shelf life for each cylinder so that the C_3H_8 concentration does not change more than $\pm$ 5 percent from its certified value. The date of gas cylinder preparation, certified C_3H_8, CO, CO_2, and CH_4 concentrations and recommended maximum shelf life must be affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards are to be used to prepare a chromatograph calibration curve as described in Section 7.2.

5.6 Span Gas. The calibration gas corresponding to 5 to 10 percent (methane or carbon equivalent) is used to span the analyzer.

6. Analyzer Performance Specifications

6.1 Linearity: $\pm$ 5 percent of the expected value for full scale settings up to the maximum percent absolute (methane or carbon equivalent) calibration point. The analyzer shall be demonstrated prior

to initial use to meet this specification through a 5-point (minimum) calibration. There shall be at least one calibration point in each of the following ranges: 5-10, 50-100, 500-1,000, 5,000-10,000, and 50,000-100,000 ppm (methane or carbon equivalent). Certification of such demonstration by the manufacturer is acceptable. An additional linearity performance check (see Section 7.2.1) must be made before each use.

6.2 Zero Drift. One percent full scale per test period.

6.3 Span Drift. One percent full scale per test period.

7. Procedure

7.1 Sampling

7.1.1 Assemble the system as shown in Figure 1. Locate the analyzer in a suitable environment. Take particular care that sample will be introduced to the system under the same conditions of pressure and flow rates as are used in calibration. For specific operating instructions for the TGNMO analyzer, refer to the operation manual.

7.1.2 Adjust the sampling system and analyzer heating system to provide a minimum temperature of 120°C and allow the system to warm up.

7.1.3 Perform a leak check as follows before sampling: Recheck to confirm that all fittings are tight. With the sample probe plugged, open the flow control valve and the excess sample bleed valve. Use leak detection fluid or immerse the tubing leading from the bleed valve in a jar of water to check that sample flow has ceased. At the conclusion of the sampling tests, recheck for leaks.

7.1.4 Begin Actual Sampling. Set the signal attenuation to yield a minimum response of 10 percent of full scale, unless the stack concentration is less than 1 ppm. Adjust the flow and bleed valves to minimize sample line residence time. Perform the analysis a minimum of four times. Report the average of the final four readings. The analyzer cycle time is normally 10 to 15 minutes.

7.1.5 At the conclusion of the sampling tests, but at least once every day, introduce zero and span gas to the analyzer to determine zero and span drifts. If the analyzer has drifted beyond the allowable performance specification, the tests shall be considered invalid.

7.2 Calibration

7.2.1 Calibration Curve. Maintain a record of performance of each item. Determine the linearity of the analyzer for TGNMO as follows: With the signal attenuation at the most sensitive setting, introduce zero gas and adjust the respectivezeroing controls to indicate a reading of less than 1 percent of full scale. With the signal attenuation at the least sensitive setting, introduce the span gas and adjust the span control to indicate the proper value on the analyzer readout. Repeat these two steps until adjustments are no longer necessary. Calculate a predicted response for the 5-10 ppm calibration gas. Introduce that calibration gas and note the value obtained. If this value is not within ± 5 percent of its predicted value, then the analyzer may need repairs, or one or both of the calibration gases may need replacement. In any event, this linearity performance specification shall be met before the analyzer is placed in actual use.

7.3 Catalyst Performance Check. These checks should be performed on a frequency established by the amount of use of the analyzer, and the nature of the organic emissions to which it is exposed. To confirm that the oxidation catalyst is functioning in the correct manner, the operator must turn off or bypass the reduction catalyst while operating the analyzer in an otherwise normal fashion. If oxidation is adequate, the only gas that will then reach the detector will be CO_2, to which the FID has no response. If responses are noted, then the oxidation catalyst must be replaced. To confirm the operation of the reduction catalyst, reverse the above procedure. If CO_2 in the calibration gases is not reduced to CH_4 as it should be, then the reduction catalyst must be replaced.

8. Calculations

8.1 Determine concentrations of TGNMO (propane equivalent) directly from the calibration curves. Multiply this number by 3 to obtain ppm TGNMO (methane or carbon equivalent).

8.2 Conversion to mass concentration values for TGNMO as carbon is made as follows:

mg TGNMO/m^3 as carbon = ppm TGNMO (methane or carbon equivalent) x 0.499

where:

$$1 \text{ ppm TGNMO (methane or carbon equivalent)} = \frac{1}{10^6} \times \frac{41.57 \text{ g-mole}}{m^3} \times \frac{12000 \text{ mg}}{\text{g-mole}} = 0.499 \text{ mg/m}^3 \text{ as carbon.}$$

where:

Molecular weight of carbon = 12

Standard conditions: 20°C, 1 atm.

9. References

9.1 Albert E. Salo, Samuel Whitz, and Robert D. MacPhee. "Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared With Flame Ionization Detectors." Presented at the 68th Annual Meeting of the Air Pollution Control Association, Boston, Ma. Paper No. 75-33.2. June 15-20, 1975.

9.2 Instruction Manual, Byron Model 401 Total Emission Analyzer, Byron Instruments, Inc., 520 1/2 S. Harrington Street, Raleigh, N.C. 27601.

ATTACHMENT 2 - DETERMINATION OF TOTAL GASEOUS NONMETHANE ORGANIC EMISSIONS AS CARBON. MANUAL SAMPLING AND ANALYSIS PROCEDURE

1. Principle and Applicability

1.1 Principle. An emission sample is anisokinetically drawn from the stack through a chilled condensate trap by means of an evacuated gas collection tank. Total gaseous nonmethane organics (TGNMO) are determined by combining the analytical results obtained from independent analyses of the condensate trap and evacuated tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide which is quantitatively collected in an evacuated vessel; a portion of the carbon dioxide is reduced to methane and measured by a flame ionization detector (FID). A portion of the sample collected in the gas sampling tank is injected into a gas chromatographic (GC) column to achieve separation of the nonmethane organics from carbon monoxide, carbon dioxide and methane; the nonmethane organics are oxidized to carbon dioxide, reduced to methane, and measured by a FID.

1.2 Applicability. This method is applicable to the measurement of total gaseous nonmethane organics in source emissions.

2. Apparatus

2.1 General. TGNMO sampling equipment can be constructed by a laboratory from commercially available components and components fabricated in a machine shop. The primary components of the sampling system are a condensate trap, flow control system, and gas sampling tank (Figure 1). The analytical system consists of two major subsystems; an oxidation system for recovery of the sample from the

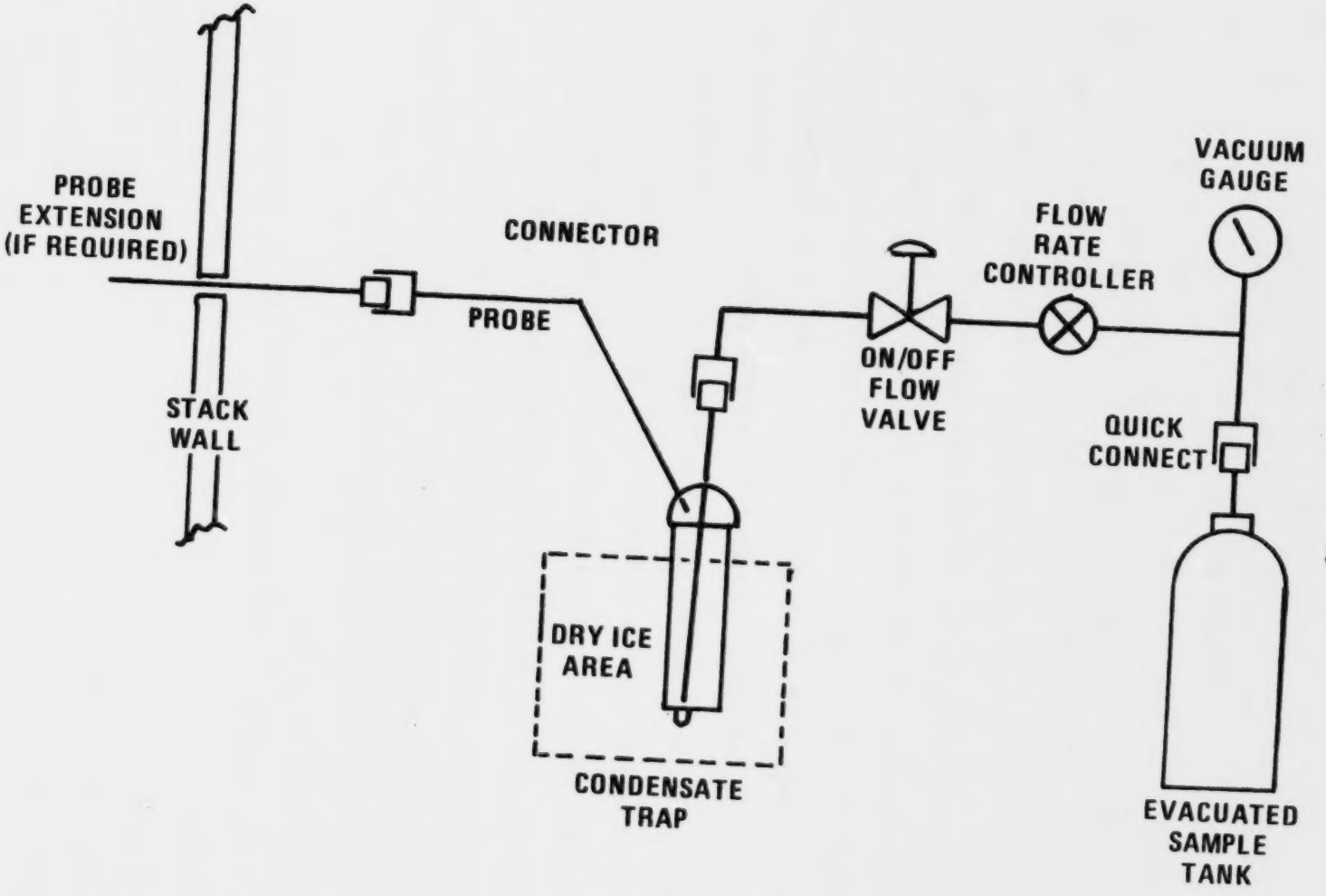

Figure 1. Sampling apparatus.

condensate trap and a TGNMO analyzer. The TGNMO analyzer is a FID preceded by a reduction catalyst, oxidation catalyst, and GC column with backflush capability (Figures 2 and 3). The system for the removal and conditioning of the organics captured in the condensate trap consists of a heat source, oxidation catalyst, nondispersive infrared (NDIR) analyzer and an intermediate gas collection tank (Figure 4).

2.2 Sampling.

2.2.1 Probe. 1/8" stainless steel tubing.

2.2.2 Condensate Trap. The condensate trap shall be constructed of 316 stainless steel; construction details of a suitable trap are shown in Figure 5.

2.2.3 Flow Shut-off Valve. Stainless steel control valve for starting and stopping sample flow.

2.2.4 Flow Control System. Any system capable of maintaining the sampling rate to within $\pm$ 10 percent of the selected flow rate (50 - 100 cc/min. range).

2.2.5 Vacuum Gauge. Vacuum gauge calibrated in mm Hg. for monitoring the vacuum of the evacuated sampling tank during leak checks and sampling.

2.2.6 Gas Collection Tank. Stainless steel or aluminum tank with a volume of 4 to 8 liters. The tank is fitted with a stainless steel female quick connect for assembly to the sampling train and analytical system.

2.2.7 Mercury manometer. U-tube mercury manometer capable of measuring pressure to within 1.0 mm Hg in the 0-900 mm range.

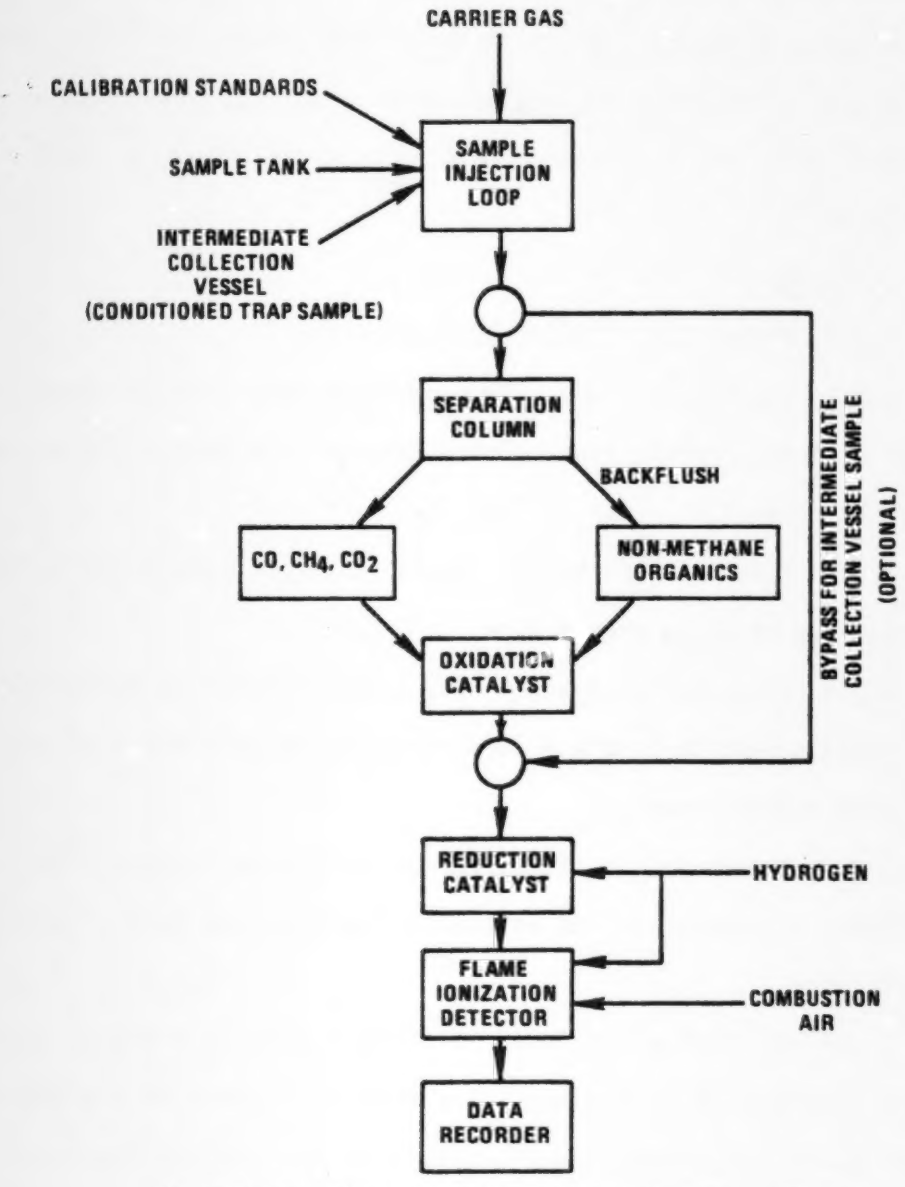

Figure 2. Simplified schematic of total gaseous non-methane organic (TGNMO) analyzer.

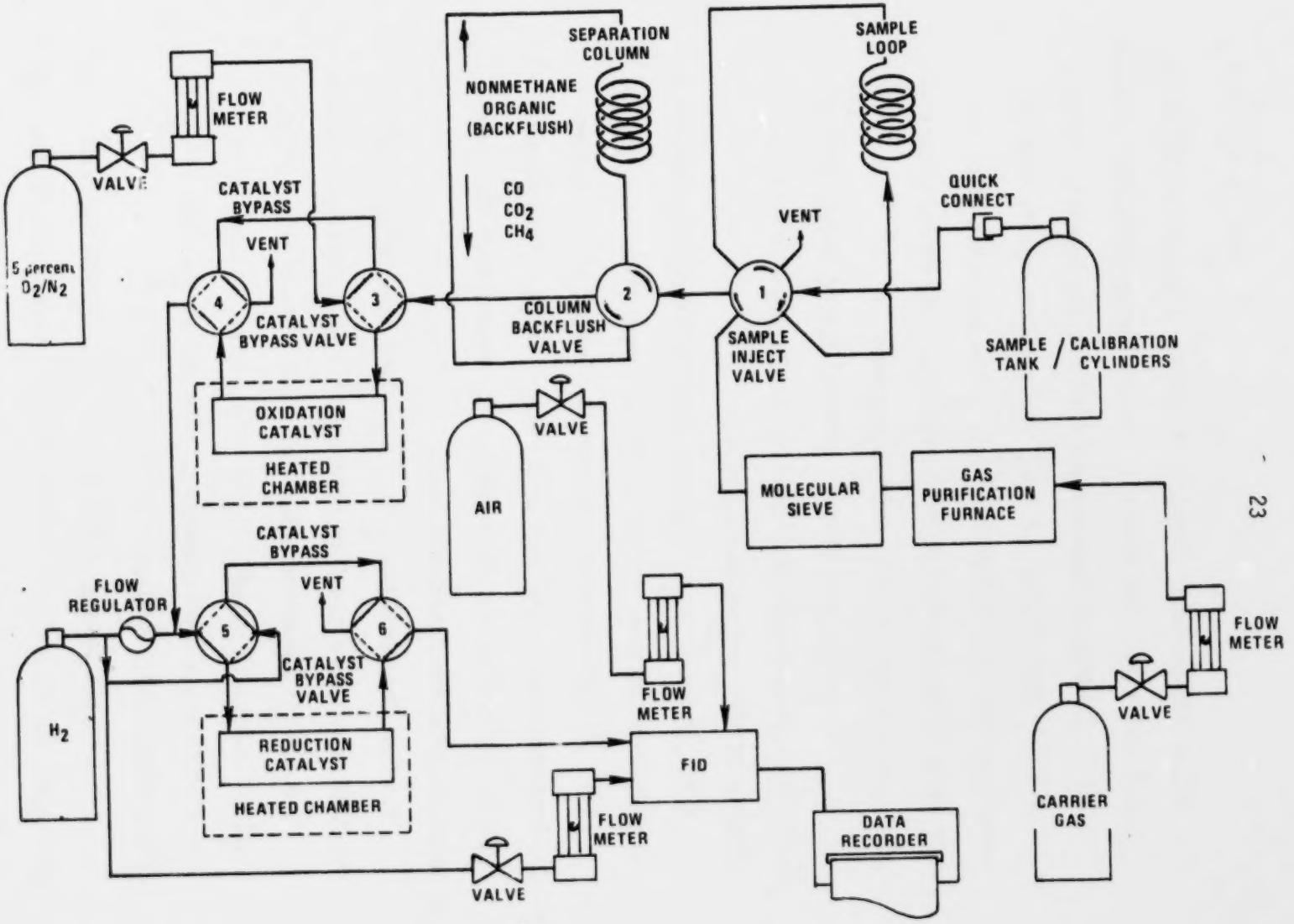

Figure 3. Total gaseous nonmethane organic (TGNMO) analyzer.

2.2.8 Vacuum Pump. Capable of pulling a vacuum of 700 mm Hg.

2.3 Analysis. For analysis, the following equipment is needed.

2.3.1 Condensate Recovery and Conditioning Apparatus (Figure 4).

2.3.1.1 Heat Source. A heat source sufficient to heat the condensate trap to a temperature just below the point where the trap turns a "cherry red" color is required. An electric muffle-type furnace heated to 600° C is recommended.

2.3.1.2 Oxidizing Catalyst. Inconel tubing packed with an oxidizing catalyst capable of meeting the catalyst efficiency criteria of this method (Section 4.4.2).

2.3.1.3 Water Trap. Any leak proof moisture trap capable of removing moisture from the gas stream may be used.

2.3.1.4 NDIR Detector. A detector capable of indicating CO_2 concentration in the zero to 5 percent range. This detector is required for monitoring the progress of combustion of the organic compounds from the condensate trap.

2.3.1.5 Pressure Regulator. Stainless steel needle valve required to maintain the NDIR detector cell at a constant pressure.

2.3.1.6 Intermediate Collection Tank. Stainless steel or aluminum collection vessel. Tanks with nominal volumes in the 1 to 4 liter range are recommended. The end of the tank is fitted with a female quick connect.

2.3.2 Total Gaseous Nonmethane Organic (TGNMO) Analyzer. Semi-continuous GC/FID analyzer capable of: (1) separating CO, CO_2, and CH_4 from nonmethane organic compounds, and (2) oxidizing the non-methane organic compounds to CO_2, reducing the CO_2 to methane, and

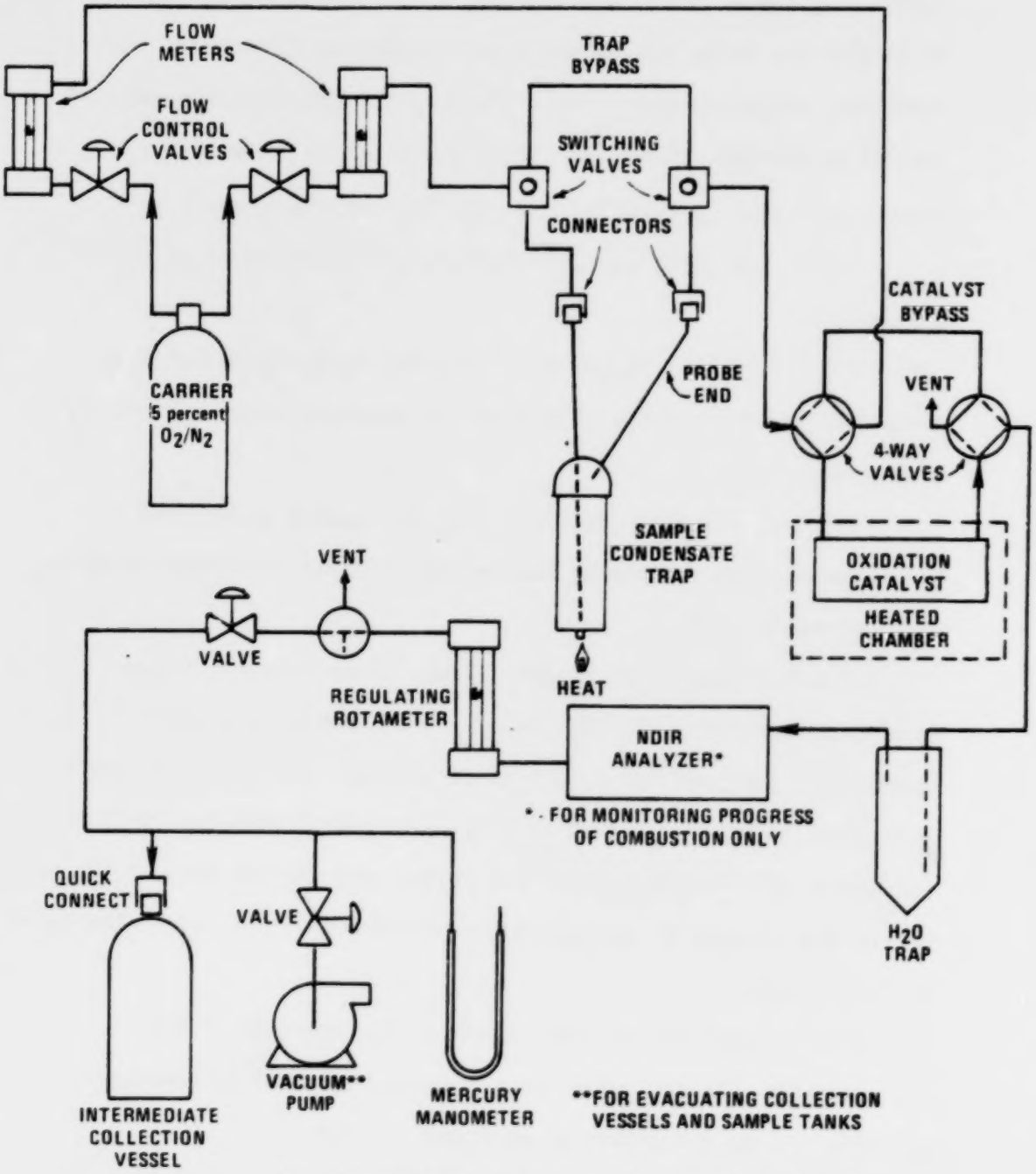

Figure 4. Condensate recovery and conditioning apparatus.

quantifying the methane. The analyzer shall be demonstrated prior to initial use to be capable of proper separation, oxidation, reduction, and measurement. As a minimum, this demonstration shall include measurement of a known TGNMO concentration present in a mixture that also contains CH_4, CO, and CO_2 (see paragraph 4.4.1).

2.3.2.1 The TGNMO analyzer consists of the following major components.

2.3.2.1.1 Oxidation Catalyst. Inconel tubing packed with an oxidation catalyst capable of meeting the catalyst efficiency criteria of paragraph 4.4.1.2.

2.3.2.1.2 Reduction Catalyst. Inconel tubing packed with a reduction catalyst capable of meeting the catalyst efficiency criteria of paragraph 4.4.1.3.

2.3.2.1.3 Separation Column. A gas chromatographic column capable of separating CO, CO_2, and CH_4 from nonmethane organic compounds. The specified column is as follows: 1/8 inch O.D. stainless steel packed with 3 feet of 10 percent methyl silicone, Sp 2100* (or equivalent) on Supelcoport* (or equivalent), 80/100 mesh, followed by 1.5 feet porapak Q* (or equivalent) 60/80 mesh. The inlet side is to the silicone.

Other columns may be used subject to the approval of the Administrator. In any event, proper separation shall be demonstrated according to the procedures of paragraph 4.4.1.4.

2.3.2.1.4 Sample Injection System. A gas chromatographic sample injection valve with sample loop sized to properly interface with the TGNMO system.

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*Mention of trade name does not constitute endorsement.

2.3.2.1.5 Flame Ionization Detector (FID). A flame ionization detector meeting the following specifications is required:

2.3.2.1.5.1 Linearity. A linearity of ±5 percent of the expected value for each full scale setting up to the maximum percent absolute (methane or carbon equivalent) calibration point is required. The FID shall be demonstrated prior to initial use to meet this specification through a 5-point (minimum) calibration. There shall be at least one calibration point in each of the following ranges: 5-10, 50-100, 500-1,000, 5,000-10,000, and 40,000-100,000 ppm (methane or carbon equivalent). Certification of such demonstration by the manufacturer is acceptable. An additional linearity performance check (see Section 4.4.1.1) must be made before each use (i.e., before each set of samples is analyzed or daily whichever occurs first).

2.3.2.1.5.2 Range. Signal attenuators shall be available so that a minimum signal response of 10 percent of full scale can be produced when analyzing calibration gas or sample.

2.3.2.1.5.3 Sensitivity. The detector sensitivity shall be equal to or better than 2.0 percent of the full scale setting, with a minimum full scale setting of 10 ppm (methane or carbon equivalent).

2.3.2.1.6 Data Recording System. Analog strip chart recorder or digital integration system for permanently recording the analytical results.

2.3.3 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1.0 mm Hg in the 0-900 mm range.

2.3.4 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm.

2.3.5 Vacuum Pump. Laboratory vacuum pump capable of evacuating the sample tanks to an absolute pressure of 5 mm Hg.

3. Reagents

3.1 Sampling.

3.1.1 Crushed Dry Ice.

3.2 Analysis.

3.2.1 TGNMO Analyzer.

3.2.1.1 Carrier Gas. Pure helium, containing less than 1 ppm organics.

3.2.1.2 Fuel Gas. Pure hydrogen, containing less than 1 ppm organics.

3.2.2 Condensate Recovery and Conditioning Apparatus.

3.2.2.1 Carrier Gas. Five percent O_2 in N_2, containing less than 1 ppm organics.

3.3 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder so that the gas concentration does not change more than $\pm$5 percent from its certified value. The date of gas cylinder preparation, certified organic concentration and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer.

3.3.1 TGNMO Analyzer.

3.3.1.1 Oxidation Catalyst Efficiency Check. Gas mixture standard with nominal concentration of 5 percent methane and 5 percent oxygen in nitrogen.

3.3.1.2 Reduction Catalyst Efficiency Check. Gas mixture standard with nominal concentration of 5 percent CO_2 in air.

3.3.1.3 Flame Ionization Detector Linearity Calibration Gases (3). Gas mixture standards with known methane (CH_4) concentrations in the 5-10 ppm, 500-1,000 ppm, and 5-10 percent range, in air. These gas standards are to be used to check the FID linearity as described in Section 4.4.1.1.

3.3.1.4 System Operation Standards (2). These calibration gases are required to check the total system operation as specified in Section 4.4.1.4. Two gas mixtures are required:

3.3.1.4.1 Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 2 percent CO_2, and 15 ppm C_3H_8, prepared in air.

3.3.1.4.2 Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 2 percent CO_2, and 1000 ppm C_3H_8, prepared in air.

3.3.2 Condensate Recovery and Conditioning Apparatus. The calibration gas specified in paragraph 3.3.1.1 is required for performing an oxidation catalyst check according to the procedure of paragraph 4.4.2.

4. Procedure

4.1 Sampling.

4.1.1 Sample Tank Evacuation. Either in the laboratory or in the field, evacuate the sample tank to 5 mm Hg absolute pressure or less (measured by a mercury U-tube manometer). Record the temperature, barometric pressure, and tank vacuum as measured by the manometer.

4.1.2 Sample Tank Leak Check. Leak check the gas sample tank immediately after the tank is evacuated. Once the tank is

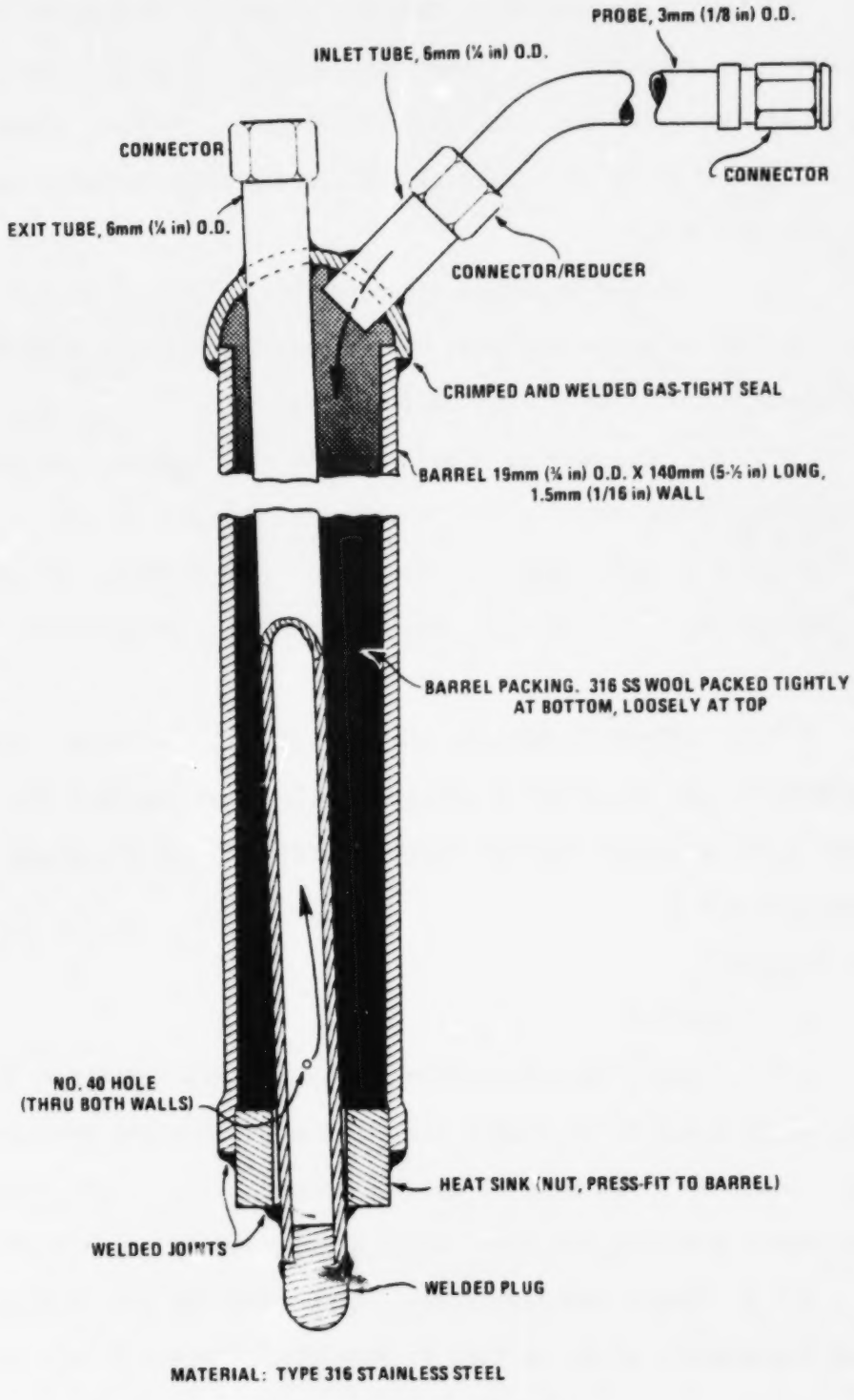
PROBE, 3mm (1/8 in) O.D.
INLET TUBE, 6mm (¼ in) O.D.
CONNECTOR
CONNECTOR
EXIT TUBE, 6mm (¼ in) O.D.
CONNECTOR/REDUCER
CRIMPED AND WELDED GAS-TIGHT SEAL
BARREL 19mm (¾ in) O.D. X 140mm (5-½ in) LONG, 1.5mm (1/16 in) WALL
BARREL PACKING. 316 SS WOOL PACKED TIGHTLY AT BOTTOM, LOOSELY AT TOP
NO. 40 HOLE (THRU BOTH WALLS)
HEAT SINK (NUT, PRESS-FIT TO BARREL)
WELDED JOINTS
WELDED PLUG
MATERIAL: TYPE 316 STAINLESS STEEL

Figure 5. Condensate trap[2].

evacuated, allow the tank to sit for 30 minutes. The tank is acceptable if no change in tank vacuum (measured by the mercury manometer) is noted.

4.1.3 Assembly. Just prior to assembly, use a mercury U-tube manometer to measure the tank vacuum. Record this vacuum (P_{ti}), the ambient temperature (T_{ti}), and the barometric pressure (P_{bi}) at this time. Assuring that the flow control valve is in the closed position, assemble the sampling system as shown in Figure 1. Immerse the condensate trap body in dry ice to within 1 or 2 inches of the point where the inlet tube joins the trap body.

4.1.4 Leak Check Procedures.

4.1.4.1 Pretest Leak Check. A pretest leak check is required. After the sampling train is assembled, record the tank vacuum as indicated by the vacuum gauge. Wait a minimum period of 15 minutes and recheck the indicated vacuum. If the vacuum has not changed, the portion of the sampling train behind the shut-off valve does not leak and is considered acceptable. To check the front portion of the sampling train, attach the leak check apparatus (Figure 6) to the probe tip. Evacuate the front half of the train (i.e., do not open the sampling train flow control valve) to a vacuum of at least 500 mm Hg. Close the shut-off valve on the leak check apparatus and record the vacuum indicated by the manometer on the data sheet (Figure 7). Allow the system to sit for 5 minutes and then recheck the vacuum. A change of less than 2 mm Hg for the 5-minute leak check period is acceptable. Record the front half leak rate (mm Hg/5-minute period) on the data form. When an acceptable leak rate has been obtained disconnect the leak check apparatus from the probe tip.

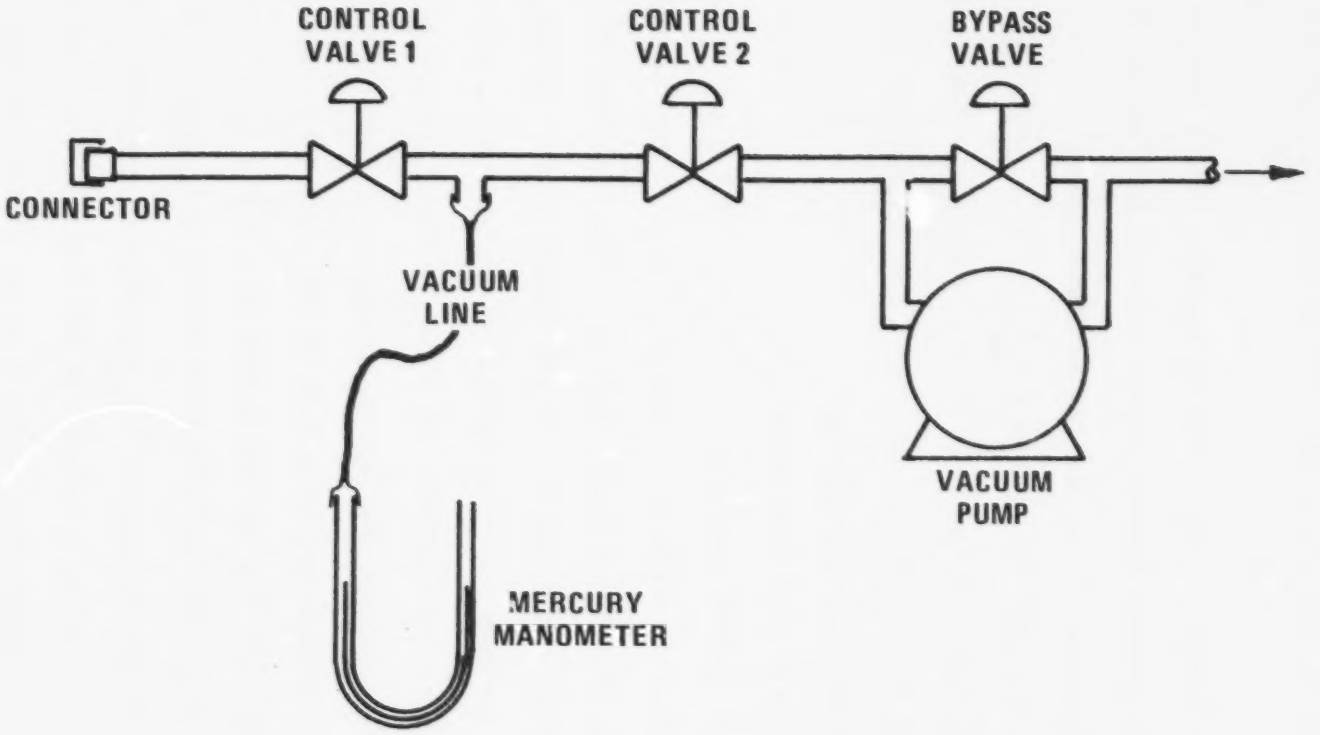

Figure 6. Leak check apparatus.

VOLATILE ORGANIC CARBON

FACILITY_____ SAMPLE LOCATION_____

LOCATION_____ OPERATOR_____

DATE_____ RUN NUMBER_____

TANK NUMBER_____ TRAP NUMBER_____ SAMPLE ID NUMBER_____

TANK VACUUM, mm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)_____ (GAUGE)_____		
POST TEST (MANOMETER)_____ (GAUGE)_____		

LEAK RATE, mm Hg/5 min.:	TANK	TRAP HALF
PRETEST		
POST TEST		

TIME CLOCK/SAMPLE	GAUGE VACUUM, mm Hg	FLOWMETER SETTING	COMMENTS

Figure 7. Example Field Data Form.

4.1.4.2 Post Test Leak Check. A leak check is mandatory at the conclusion of each test run. After sampling is completed, attach the U-tube manometer to the probe tip; minimize the amount of flexible line used. Open the sample train flow control valve for a period of 2 minutes or until the vacuum indicated on the manometer stabilizes, whichever occurs first; shut off the sample train flow control valve. Record the vacuums indicated on the manometer (front half) and on the tank vacuum gauge (backhalf). After 5 minutes, recheck these vacuum readings. A leak rate of less than 2 mm Hg per 5-minute period is acceptable for the front half; the back half portion is acceptable if no visible change in the tank vacuum gauge occurs. Record the post test leak rate (mm Hg per 5 minutes), and then disconnect the manometer from the probe tip and seal the probe. If the sampling train does not pass the post test leak check, invalidate the run.

4.1.5 Sample Train Operation. Place the probe into the stack such that the probe is perpendicular to the direction of stack gas flow; locate the probe tip at a single preselected point. For stacks having a negative static pressure, assure that the sample port is sufficiently sealed to prevent air in-leakage around the probe. Check the dry ice level and add ice if necessary. Record the clock time and sample tank gauge vacuum. To begin sampling, open and adjust (if applicable) the flow control valve(s) of the flow control system utilized in the sampling train; maintain a constant flow rate ($\pm$10 percent) throughout the duration of the sampling period. Record the gauge vacuum and flowmeter setting (if applicable) at 5-minute intervals.

Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulation; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained. When the sampling is completed, close the gas sampling tank control valve. Record the final readings. Note: If the sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After removing the probe from the stack, remove the evacuated tank from the sampling train (without disconnecting other portions of the sampling train) and connect another evacuated tank to the sampling train. Prior to attaching the new tank to the sampling train, assure that the tank vacuum (measured on-site by the U-tube manometer) has been recorded on the data form and that the tank has been leak-checked (on-site). After the new tank is attached to the sample train, proceed with the sampling; after the required minimum sampling time has been exceeded, end the test.

4.2 Sample Recovery. After sampling is completed, remove the probe from the stack and seal the probe end. Conduct the post test leak check according to the procedures of paragraph 4.1.4.2. After the post test leak check has been conducted, disconnect the condensate trap at the flow metering system. Tightly seal the ends of the condensate trap; keep the trap packed in dry ice until analysis. Remove the flow metering system from the sample tank. Attach the U-tube manometer to the tank (keep length of flexible connecting line to a minimum)

and record the final tank vacuum (P_t); record the tank temperature (T_t) and barometric pressure at this time. Disconnect the manometer from the tank. Assure that the test run number is properly identified on the condensate trap and evacuated tank(s).

4.3 Analysis.

4.3.1 Preparation.

4.3.1.1 TGNMO Analyzer. Set the carrier gas, air, and fuel flow rates and then begin heating the catalysts to their operating temperatures. Conduct the calibration linearity check required in paragraph 4.4.1.1 and the system operation check required in paragraph 4.4.1.4. Optional: Conduct the catalyst performance checks required in paragraphs 4.4.1.2 and 4.4.1.3 prior to analyzing the test samples.

4.3.1.2 Condensate Recovery and Conditioning Apparatus. Set the carrier gas flow rate and begin heating the catalyst to its operating temperature. Conduct the catalyst performance check required in paragraph 4.4.2 prior to oxidizing any samples.

4.3.2 Condensate Trap Carbon Dioxide Purge and Evacuated Sample Tank Pressurization. The first step in analysis is to purge the condensate trap of any CO_2 which it may contain and to simultaneously pressurize the gas sample tank. This is accomplished as follows: Obtain both the sample tank and condensate trap from the test run to be analyzed. Set up the condensate recovery and conditioning apparatus so that the carrier flow bypasses the condensate trap hook-up terminals, bypasses the oxidation catalyst, and is vented to the atmosphere. Next, attach the condensate trap to the apparatus and pack the trap in dry

ice. Assure that the valve isolating the collection vessel connection from the atmospheric vent is closed and then attach the gas sample tank to the system as if it were the intermediate collection vessel. Record the tank vacuum on the laboratory data form. Assure that the NDIR analyzer indicates a zero output level and then switch the carrier flow through the condensate trap; immediately switch the carrier flow from vent to collect and open the valve to the tank. The condensate trap recovery and conditioning apparatus should now be set up as indicated in Figure 8. Monitor the NDIR; when CO_2 is no longer being passed through the system, switch the carrier flow so that it once again bypasses the condensate trap. Continue in this manner until the gas sample tank is pressurized to a nominal gauge pressure of 800 mm mercury. At this time, isolate the tank, vent the carrier flow, and record the sample tank pressure (P_{tf}), barometric pressure (P_{bf}), and ambient temperature (T_{tf}). Remove the gas sample tank from the system.

4.3.3 Recovery of Condensate Trap Sample. Oxidation and collection of the sample in the condensate trap is now ready to begin. From the step just completed in paragraph 4.3.2 above, the system should be set up so that the carrier flow bypasses the condensate trap, bypasses the oxidation catalyst, and is vented to the atmosphere. Attach an evacuated intermediate collection vessel to the system and then, switch the carrier so that it flows through the oxidation catalyst. Monitor the NDIR and assure that the analyzer indicates a zero output level. Switch the carrier from vent to collect and open the collection tank valve; remove the dry ice from the trap and then switch the carrier flow through the trap. The system should now be set up to operate as indicated in Figure 9.

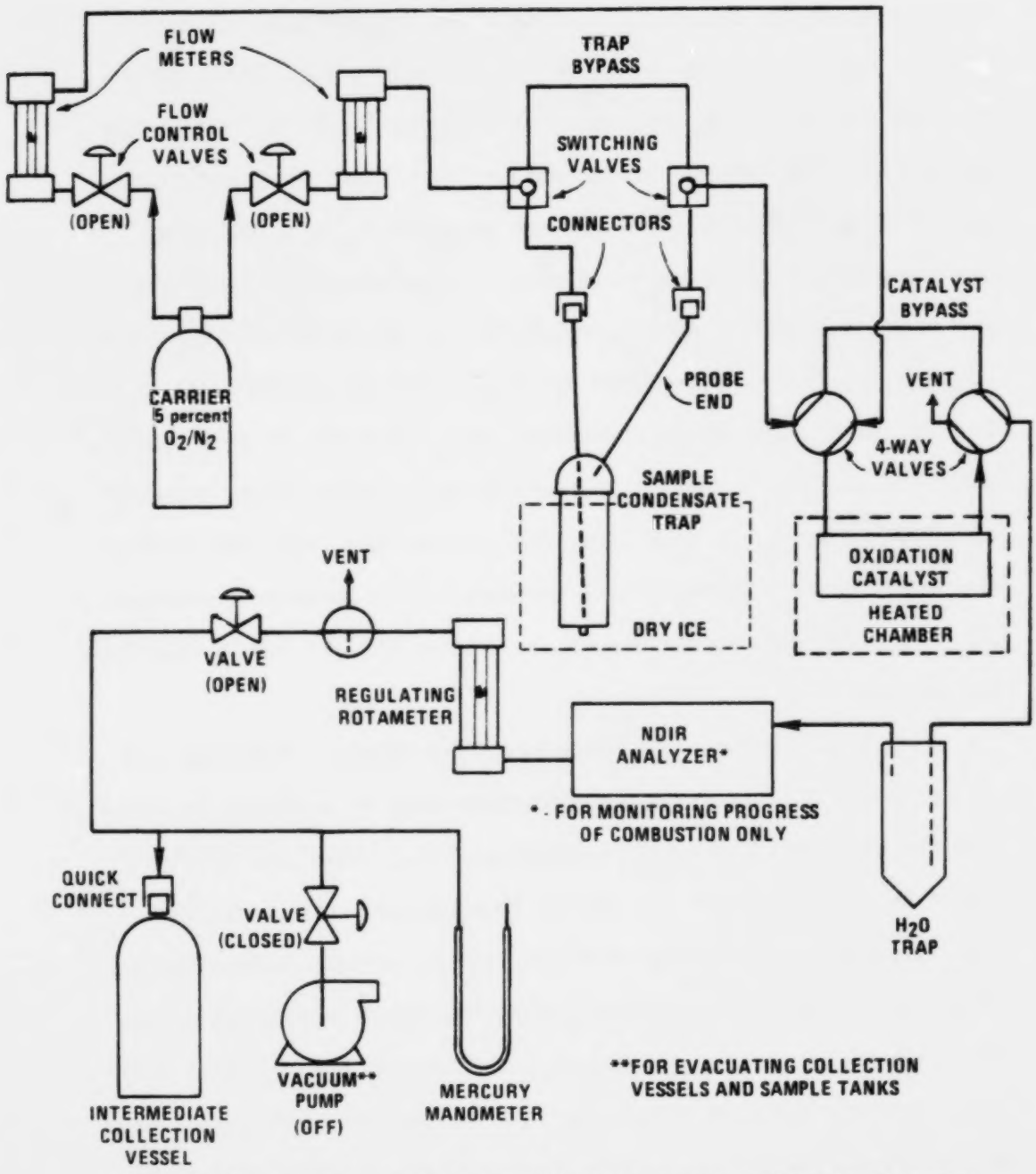

Figure 8. Condensate recovery and conditioning apparatus, carbon dioxide purge.

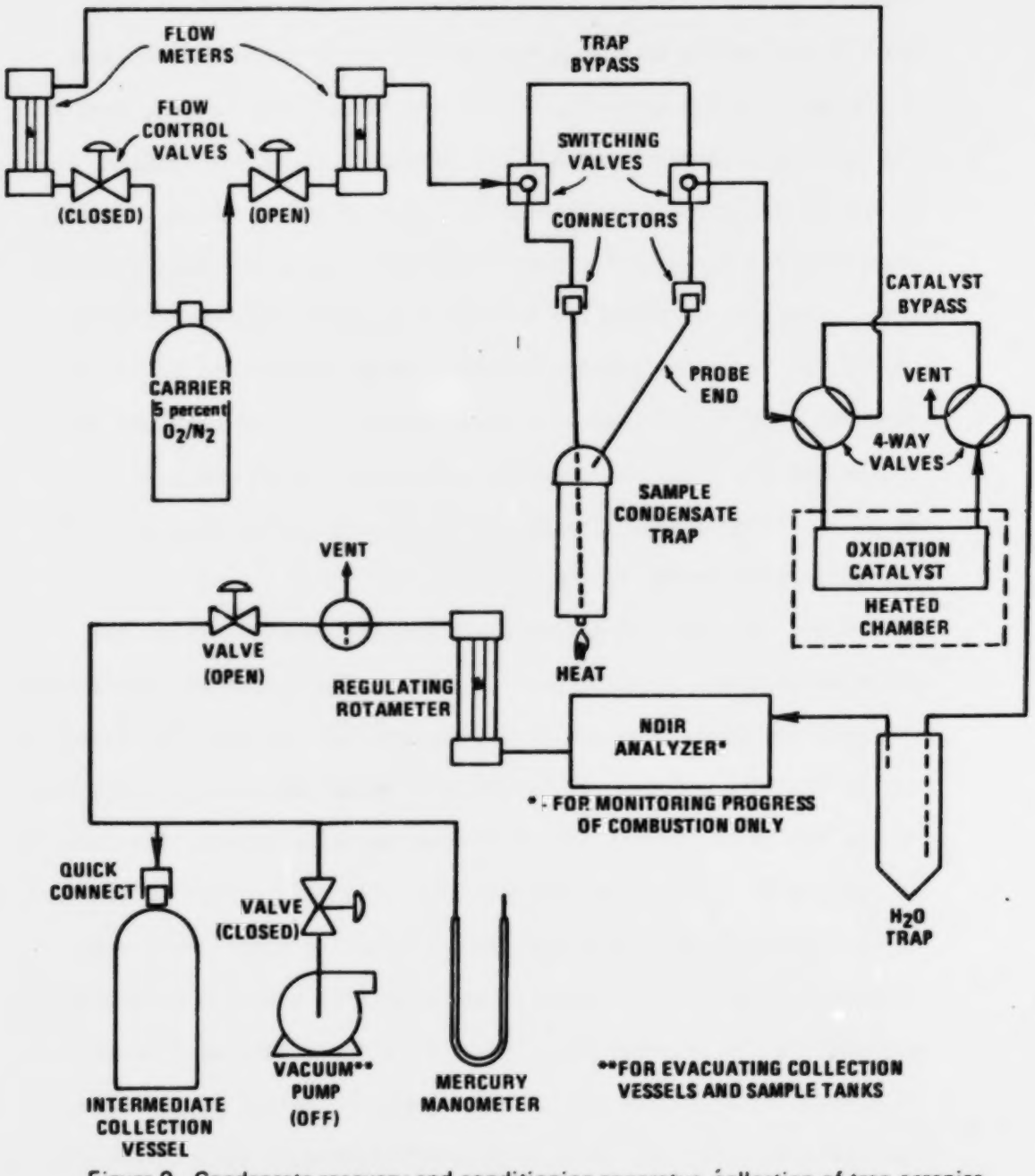

Figure 9. Condensate recovery and conditioning apparatus, collection of trap organics.

Begin heating the condensate trap. The trap should be heated to a temperature at which the trap glows a "dull red" (approximately 600° C) and should be maintained at this temperature for at least 5 minutes. During oxidation of the condensate trap sample, monitor the NDIR to determine when all the sample has been removed and oxidized (indicated by return to baseline of NDIR analyzer output). When complete recovery has been indicated, remove the heat from the trap. However, continue the carrier flow until the intermediate collection vessel is pressurized to a gauge pressure of 800 mm Hg (nominal). When the vessel is pressurized, vent the carrier; measure and record the final intermediate collection vessel pressure (P_f) as well as the barometric pressure (P_{bv}), ambient temperature (T_v), and collection vessel volume (V_v).

4.3.4 Analysis of Recovered Condensate Sample. After the preparation steps in paragraph 4.3.1 have been completed, the analyzer is ready for conducting analyses. Assure that the analyzer system is set so that the carrier gas is routed through the reduction catalyst to the FID (flow through the separation column and oxidation catalyst is optional). Attach the intermediate collection vessel to the tank inlet fitting of the TGNMO analyzer. Purge the sample loop with sample and then inject a preliminary sample in order to determine the appropriate FID attenuation. Inject triplicate samples from the intermediate collection vessel and record the values (C_{cm}). When appropriate, check the instrument calibration according to the procedures of paragraph 4.4.1.4.

4.3.5 Analysis of Gas Sample Tank. Assure that the analyzer is set up so that the carrier flow is routed through the separation

column as well as both the oxidation and reduction catalysts. During analysis for the nonmethane organics the separation column is operated as follows: First, operate the column at -78° C (dry ice temperature) to elute the CO and CH_4. After the CH_4 peak, operate the column at 0° C to elute the CO_2. When the CO_2 is completely eluted, switch the carrier flow to backflush the column and simultaneously raise the column temperature to 100° C in order to elute all nonmethane organics. (Exact timings for column operation are determined from the calibration standard). Attach the gas sample tank to the tank inlet fitting of the TGNMO analyzer. Purge the sample loop with sample and inject a preliminary sample in order to determine the appropriate FID attenuation for monitoring the backflushed non-methane organics. Inject triplicate samples from the gas sample tank and record the values obtained for the nonmethane organics (C_{tm}). When appropriate, check the instrument calibration according to the procedures of paragraph 4.4.1.4.

4.4 Calibration. Maintain a record of performance of each item.

4.4.1 TGNMO Analyzer.

4.4.1.1 FID Calibration and linearity check. Set up the TGNMO system so that the carrier gas bypasses the oxidation and reduction catalysts. Zero and span the FID by injecting samples of the high value (5-10 percent) calibration gas (paragraph 3.3.1.3) and adjusting the instrument output to the correct level. Then check the instrument linearity by injecting triplicate samples of the low (5-10 ppm) and mid-range (500-1,000 ppm) calibration gases (paragraph 3.3.1.3). The system linearity is acceptable if the results (average for triplicate samples of each gas) are within $\pm$ 5 percent of the

expected values. This calibration and linearity check shall be conducted prior to analyzing each set of samples (i.e., samples from a given source test).

4.4.1.2 Oxidation Catalyst Efficiency Check. This check should be performed on a frequency established by the amount of use of the analyzer and the nature of the organic emissions to which the catalyst is exposed. As a minimum, perform this check prior to putting the analyzer into service.

To confirm that the oxidation catalyst is functioning in a correct manner, the operator must turn off or bypass the reduction catalyst while operating the analyzer in an otherwise normal fashion. Inject triplicate samples of the methane standard gas (paragraph 3.3.1.1) into the system. If oxidation is adequate, the only gas that will then reach the detector will be CO_2, to which the FID has no response. If a response is noted, the oxidation catalyst must be replaced.

4.4.1.3 Reduction Catalyst Efficiency Check. This check should be performed on a frequency established by the amount of use of the analyzer. As a minimum, perform this check prior to putting the analyzer into service. To confirm proper operation of the reduction catalyst, the operator must bypass the oxidation catalyst while operating the analyzer in an otherwise normal manner. After setting the carrier flow to bypass the oxidation catalyst, inject triplicate samples of the carbon dioxide standard gas (Section 3.3.1.2). The catalyst operation is acceptable if the average response of the triplicate CO_2 sample injections is within $\pm$ 2 percent of the expected value and no one CO_2 sample injection varies by more than $\pm$ 5 percent from the expected value.

4.4.1.4 System Operation Check. This system check should be conducted at a frequency consistent with the amount of use and the reliability of the particular analyzer. As a minimum, this system check shall be conducted before and after each set of emission samples is analyzed. If this system check is not successfully completed at the conclusion of the analyses, the results shall be invalidated. Operate the TGNMO analyzer in a normal fashion, passing the carrier flow through the separation column and both the oxidation and reduction catalysts. Inject triplicate samples of the two mixed gas standards specified in Section 3.3.1.4. The system operation is acceptable if, for each gas mixture, the average non-methane organic value for the triplicate samples is within $\pm$ 3 percent of the expected value and no one sample analysis varies by more than $\pm$ 5 percent from the average value for the triplicate samples.

4.4.2 Condensate Trap Recovery and Conditioning Apparatus Oxidation Catalyst Check. This catalyst check should be conducted at a frequency consistent with the amount of use of the catalyst, as well as, the nature and concentration level of the organics being recovered by the system. As a minimum, perform this check prior to and immediately after conditioning each set of emission sample traps.

Set up the condensate trap recovery system so that the carrier flow bypasses the trap inlet and is vented to the atmosphere at the system outlet. Assure that the tank collection valve is closed and then attach an evacuated intermediate collection vessel to the system. Connect the methane standard gas cylinder (Section 3.3.1.1) to the system's condensate trap connector (probe end, figure 4). Adjust the

system valving so that the standard gas cylinder acts as the carrier gas; switch off the carrier and use the cylinder of standard gas to supply a gas flow rate equal to the carrier flow normally used during trap sample recovery. Now switch from vent to collect in order to begin collecting a sample. Continue collecting a sample in the normal manner until the intermediate vessel is filled to a nominal pressure of 300 mm Hg. Remove the intermediate vessel from the system and vent the carrier flow to the atmosphere. Switch the valving to return the system to its normal carrier gas and normal operating conditions. Set up the TGNMO analyzer to operate with the oxidation and reduction catalysts bypassed. Inject a sample from the intermediate collection vessel into the analyzer. The operation of the condensate trap recovery system oxidation catalyst is acceptable if oxidation of the standard methane gas was 99.5 percent complete, as indicated by the response of the TGNMO analyzer FID.

4.4.3 Gas Sampling Tank. The volume of the gas sampling tanks used must be determined. Prior to putting each tank in service, determine the tank volume by weighing the tanks empty and then filled with water; weigh to the nearest 0.5 gm and record the results.

4.4.4 Intermediate Collection Vessel. The volume of the intermediate collection vessels used to collect CO_2 during the analysis of the condensate traps must be determined. Prior to putting each vessel into service, determine the volume by weighing the vessel empty and then filled with water; weigh to the nearest 0.5 gm and record the results.

5. Calculations.

Note: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge pressure.

5.1 Sample Volume. For each test run, calculate the gas volume sampled.

$$V_s = 0.386V\left[\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}\right]$$

5.2 Noncondensible Organics. For each collection tank, determine the concentration of nonmethane organics (ppm C):

$$C_t = \frac{1}{r}\left[\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}}\right]\sum_{j=1}^{r} C_{tm_j}$$

5.3 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C):

$$C_c = \frac{0.386}{N}\,\frac{V_v}{V_s}\,\frac{P_f}{T_f}\sum_{k=1}^{n} C_{cm_k}$$

5.4 Total Gaseous Nonmethane Organics (TGNMO). To determine the TGNMO concentration for each test run, use the following equation:

$$C = C_t + C_c$$

Where:

C = Total gaseous nonmethane organic (TGNMO) concentration of the effluent, ppm carbon equivalent.

C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm carbon equivalent.

C_{cm} = Measured concentration (TGNMO analyzer) for the condensate trap (intermediate collection vessel), ppm methane.

C_t = Calculated noncondensible organic concentration of the effluent, ppm carbon equivalent.

C_{tm} = Measured concentration (TGNMO analyzer) for gas collection tank sample, ppm methane.

P_f = Final pressure of intermediate collection vessel, mm Hg., absolute.

P_{ti} = Gas sample tank pressure prior to sampling, mm Hg, absolute.

P_t = Gas sample tank pressure after sampling, but prior to pressurizing, mm Hg, absolute.

P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg, absolute.

T_f = Final temperature of intermediate collection vessel, ^{o}k.

T_{ti} = Gas sample tank temperature prior to sampling, ^{o}k.

T_t = Gas sample tank temperature at completion of sampling, ^{o}k.

T_{tf} = Gas sample tank temperature after pressurizing, ^{o}k.

V = Gas collection tank volume, dscm.

V_v = Intermediate collection tank volume, dscm.

V_s = Gas volume sampled, dscm.

r = Total number of analyzer injections of tank sample during analysis (where j = injection number, 1 . . .r)

n = Total number of analyzer injections of condensible inter-

mediate collection vessel during analysis (where k = injection number, 1 . . .n).

Standard Conditions = Dry, 760 mm Hg, 293° K.

6. Bibliography

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6.2 Albert E. Salo, William L. Oaks, Robert D. MacPhee. "Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control." Presented at the 67th Annual Meeting of the Air Pollution Control Association, Denver, Colorado, Paper No. 74-190, June 9-13, 1974.

ATTACHMENT 3. ALTERNATE TEST METHOD FOR DIRECT MEASUREMENT OF TOTAL GASEOUS ORGANIC COMPOUNDS USING A FLAME IONIZATION ANALYZER

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the performance characteristics of the flame ionization detector, nor by those who are unfamiliar with source sampling.

1. Principle and Applicability

1.1 Principle. The sample is drawn from the source, through a heated sample line and glass fiber filter to a flame ionization analyzer (FIA). Ions formed in the combustion of a specific hydrocarbon compound in a H_2 - O_2 flame establish a current that is proportional to the mass flow rate of that hydrocarbon to the flame. This current is collected at two polarized electrodes, and is read out on a potentiometric recorder and compared with a calibration curve based on propane (C_3H_8), or an organic solvent, as appropriate. The results are reported as equivalents of methane (CH_4) or carbon, or in terms of an organic solvent.

1.2 Applicability. This method is applicable for the determination of the true carbon mass concentration, and/or an indicated volume or mass concentration (expressed in terms of carbon or of an assumed organic compound, e.g., methane equivalent) of gaseous organic compounds present in an emission stream. It can also be used to measure the mass concentration of an organic solvent if stable mass standards of the solvent can be generated.

The measurement will not exclude methane, so a supplemental measurement of methane may be necessary.

2. Range and Sensitivity

2.1 Range. Signal attenuators shall be available so that a minimum signal response of 10 percent of full scale can be produced when analyzing calibration gas or sample.

2.2 Sensitivity. The detector sensitivity shall be equal to or better than 2.0 percent of the full scale setting, with a minimum full scale setting of 10 ppm (methane or carbon equivalent).

3. Interferences

3.1 Nonorganic Gases. There is no response to nitrogen, carbon monoxide, carbon dioxide, or water vapor. However, the analyzer response to organics will be affected by the composition of the background or carrier gas. It is, therefore, required that the calibration gases be contained in air, which is most likely to be the same carrier gas as that of the actual sample.

Investigation of a reported oxygen synergism[2] has shown that a 40/60 mixed fuel (40 percent H_2, 60 percent He) is required if the oxygen content of the emission stream varies more than a few percent from its mean value. Mixed fuel will also be required if the oxygen content of the emission stream varies more than a few percent from the oxygen content of the calibration gases.

3.2 Organic compounds. Acetylenic compounds give a slightly higher response than aliphatic compounds. Carbon atoms bound to oxygen, nitrogen, or halogens give a reduced or zero response.

Table 1[3] illustrates these effects in terms of the relative response of one FIA to various hydrocarbons. The response is shown as effective carbon number (ECN), as follows:

$$ECN = \frac{\text{Instrument response caused by atom of given type}}{\text{Instrument response caused by aliphatic carbon atom}}$$

These values are true for one mode of operation of a specific detector under specific conditions (e.g., mixed N_2, H_2 fuel). It has been reported that these numbers may vary widely for different operating conditions and for different detectors. Variations of as much as 25 percent have been observed in studies of the types of organics associated with automotive emissions. The variation was observed to decrease with decreasing sample flow rate, but with an accompanying decrease in sensitivity.[7]

TABLE 1. APPROXIMATE EFFECTIVE CARBON NUMBERS (FROM BECKMAN INSTRUMENTS)

Type of Atom	Occurrence	Effective Carbon Number
Carbon	In Aliphatic Compound	+1.0
Carbon	In Aromatic Compound	+1.0
Carbon	In Olefinic Compound	+0.95
Carbon	In Acetylenic Compound	+1.30
Carbon	In Carbonyl Radical	0.0
Carbon	In Nitrite	+0.3
Oxygen	In Ether	-1.0

TABLE 1. APPROXIMATE EFFECTIVE CARBON NUMBERS
(FROM BECKMAN INSTRUMENTS)
(Continued)

Type of Atom	Occurrence	Effective Carbon Number
Oxygen	In Primary Alcohol	-0.6
Oxygen	In Secondary Alcohol	-0.75
Oxygen	In Tertiary Alcohol, Ester	-0.25
Chlorine	As two or more chlorine atoms on single aliphatic carbon atom	-0.12 each
Chlorine	In Olefinic Carbon Atom	+0.05
Nitrogen	In Amine	Value similar to that for oxygen atom in corresponding alcohol

From this information it can be seen that the accuracy of this method for a given source will be largely dependent on the particular makeup of organic emissions from the source.

3.3 Other effects. Significant changes in viscosity of the emission gas from that of the calibration gas will affect the mass rate of organics to the detector. If this phenomena is expected to occur, a corrective technique must be devised.

If the instrument is calibrated with organic solvent standards, and then used to measure emissions of that solvent, their response variations have been calibrated out.

4. Apparatus

4.1 Commercially available heated FIA. The analyzer should

be demonstrated, preferably by the manufacturer, or his representative, to meet or exceed manufacturer's specifications and those described in this method. The entire sampling and analysis system as encountered by gaseous organics must be capable of being maintained in the temperature range of 350 to 440°F, or less, consistent with the emission regulation.

4.2 Sample conditioning or interface system. Probe with filter, Teflon* sample line, Teflon-coated diaphragm pump or stainless steel bellows pump and Teflon flow control valves, capable of being maintained in the temperature range of 350 to 400°F, or less, consistent with the emission regulation.

4.3 Potentiometric Recorder (optional). Strip chart recorder with a voltage output compatible with the FIA.

5. Reagents

5.1 Fuel. A hydrogen and helium mixture containing less than 2 ppm organics (methane or carbon equivalent).

5.2 Combustion Air. High purity air with less than 2 ppm organics (methane or carbon equivalent). Required only if the emission stream does not contain sufficient oxygen.

5.3 Zero Gas. Less than 0.1 ppm organics (methane or carbon equivalent).

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* Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

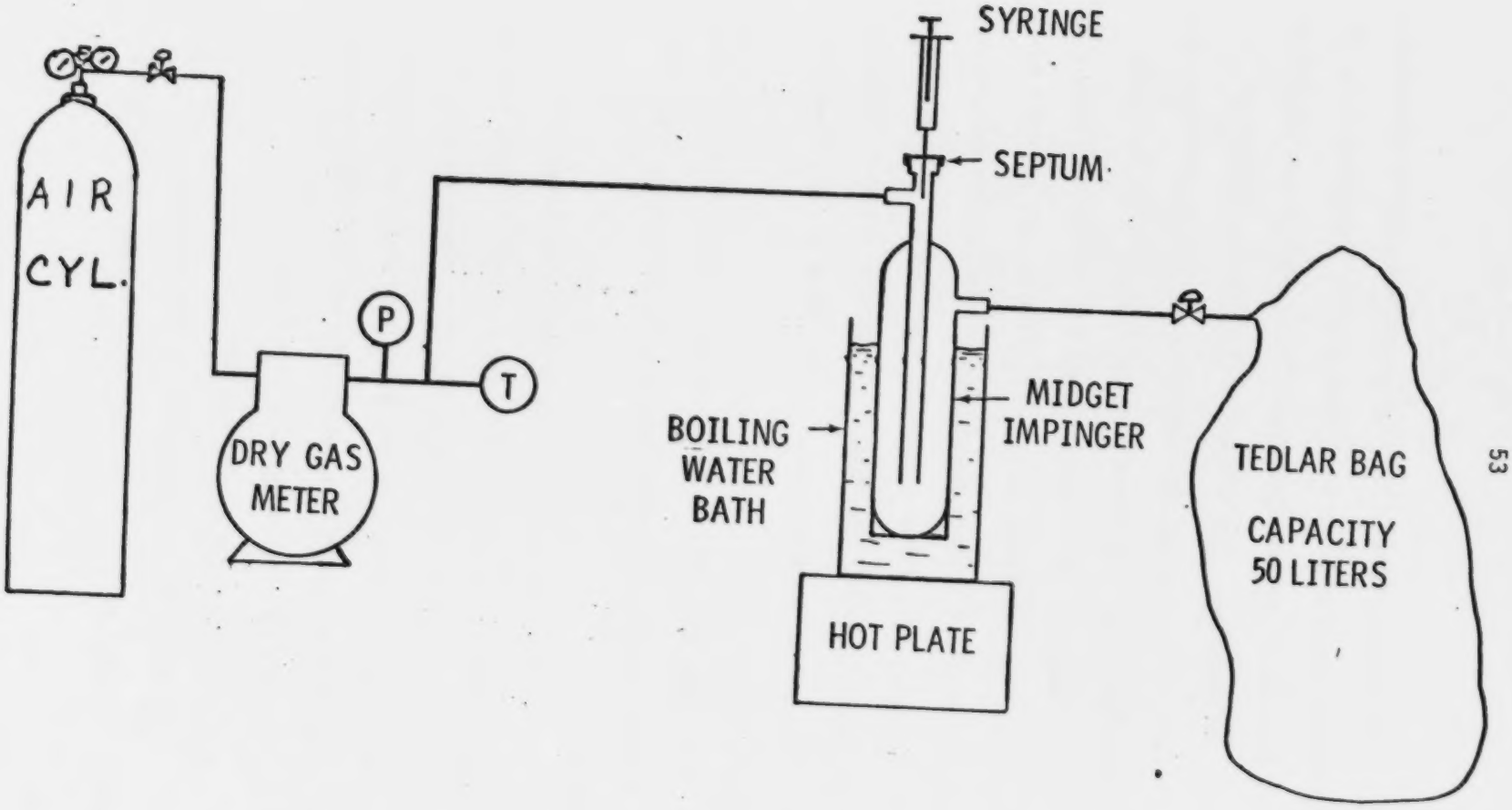

FIGURE 2. PREPARATION OF SOLVENT STANDARDS

5.4 Calibration Gases (2). Gas mixture standards with known concentrations corresponding to ranges of 5 to 10 ppm and 5 to 10 percent (methane or carbon equivalent) are prepared and certified by a gas manufacturer. The mixture will normally consist of C_3H_8 in air. Other organic(s) can be used, if appropriate. The gas manufacturer must recommend a maximum shelf life for each cylinder so that the concentration does not change more than $\pm$ 5 percent from the certified value. The date of gas cylinder preparation, certified propane concentration and recommended maximum shelf life must be affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards are to be used to prepare a calibration curve as described in Section 7.2.

5.5 Span Gas. The calibration gas corresponding to 5 to 10 percent (methane or carbon equivalent) is used to span the analyzer.

5.6 Organic Solvent. Either a sample obtained from the solvent source, or a sample distilled from paint, ink, etc. in accordance with ASTM Procedure D3272-73T. Required only if unaltered solvent emissions are being measured, mass calculations in terms of the solvent are necessary, and the relative response factor of the FIA to the solvent is unknown.

6. System Performance Specifications

6.1 Linearity. $\pm$ 5 percent of the expected value for full scale settings up to the maximum percent absolute (methane or

carbon equivalent) calibration point. The analyzer shall be demonstrated prior to initial use to meet this specification through a 5-point (minimum) calibration. There shall be at least one calibration point in each of the following ranges: 5-10, 50-100, 500-1,000, 5,000-10,000, and 50,000-100,000 ppm (methane or carbon equivalent). Certification of such demonstration by the manufacturer is acceptable. An additional linearity performance check (see Section 7.2.1) must be made before each use.

6.2 Zero Drift. One percent full scale per test period.

6.3 Span Drift. One percent full scale per test period.

7. Procedure

7.1 Sampling.

7.1.1 Assemble the systems as shown in Figure 1. Locate the FIA in a suitably protected environment. Take particular care that sample will be introduced to the FIA under the same conditions of pressure and flow rates as are used in calibration. For specific operating instructions for the FID, refer to manufacturer's manual.

7.1.2 Adjust the sample conditioning and analyzer heating systems to provide a temperature of 350 to 400°F, or less, consistent with the emission regulation, and allow the systems to warm up.

7.1.3 Perform a leak check as follows before sampling. Recheck to confirm that all fittings are tight. With the sample

probe plugged, open the flow control valve and the excess sample bleed valve. Use leak detection fluid or immerse the tubing leading from the bleed valve in a jar of water to check that sample flow has ceased. At the conclusion of the sampling tests, recheck for leaks.

7.1.4 Begin Actual Sampling. Set the signal attenuation to yield a minimum response of 10 percent of full scale unless the stack concentration is less than 1 ppm. Adjust the flow and bleed valves to minimize sample line residence time. Compare instrument readings with the calibration curve to obtain emission concentrations based on the calibration gas.

7.1.5 At the conclusion of the sampling tests, but at least once every day, introduce zero and span gases to the analyzer to determine zero and span drifts. If the analyzer has drifted beyond the allowable performance specification, the tests shall be considered invalid.

7.2 Calibration and Solvent Standards.

7.2.1 Calibration Curve. Maintain a record of performance of each item. Determine the linearity of the analyzer as follows: With the signal attenuation at the most sensitive setting, introduce zero gas and adjust the respective zeroing controls to indiate a reading of less than 1 percent of full scale. With the signal attenuation at the least sensitive setting, introduce the span gas and adjust the span control to indicate the proper value on the analyzer readout. Repeat these

two steps until adjustments are no longer necessary. Calculate a predicted response for the 5 to 10 ppm calibration gas. Introduce that calibration gas and note the value obtained. If the value is not within ± 5 percent of its predicted value, then the analyzer may need repairs, or one or both of the calibration gases may need replacement. In any event, this linearity performance specification shall be met before the analyzer is placed in actual use.

7.2.2 Preparation of Solvent Standard Gas Mixtures. (Optional--see Sections 1.2 and 5.6). Assemble the apparatus shown in Figure 2. Evacuate a 50-liter Tedlar or aluminized Mylar bag that has passed a leak check (described in Section 7.2.2.1) and meter in about 50 liters of air. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. While the bag is filling use the 10 µl syringe to inject 10 µl of the solvent through the septum on top of the impinger. This gives a concentration of approximately 200 µg/liter. In a like manner, use the other syringe to prepare dilutions having approximately 40 and 20 µg/liter concentrations. To calculate the specific concentrations, refer to Section 8.1. These gas mixture standards may be used for a few days from the date of preparation, as determined by repetitive analysis for concentration degradation. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

7.2.2.1 Solvent Standards Bag Leak Checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows: to leak check, connect a water manometer and pressurize the bag to 5-10 cm H_2O (2-4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: an alternative leak check method is to pressurize the bag to 5-10 cm H_2O or 2-4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations

All measurements or calculations must be corrected for CH_4, if required by the emission regulation.

8.1 Carbon or Surrogate Organic Compound Concentration.

8.1.1 Volume concentration [ppm]. To determine emission concentrations of total gaseous organics (wet basis) on a CH_4 or carbon equivalent basis, multiply the recorded emission values by the number of carbon atoms in a molecule of calibration gas. In some instances it will be required to report emissions on the basis of the calibration gas, in which case no calculations are necessary.

8.1.2 Mass concentration [mg/m^3]. To convert volume concentration to mass concentration, proceed as follows:

8.1.2.1 Establish Standard Conditions. Find the volume occupied by 1 mg. mole of ideal gas at these conditions. Then find the number of mg. moles in 1 m^3 (at saturation).

8.1.2.2 Determine the molecular weight of the assumed organic compound in which the emission is to be expressed.

8.1.2.3 Use the values obtained in 8.1.2.1 and 8.1.2.2 to determine the mass concentration (mg/m^3) at saturation. Divide this number by 10^6 to find the mg/m^3 equivalent to 1 ppm.

8.1.2.4 Multiply the result obtained in 8.1.2.3 by the volume concentration obtained in 8.1.1. The result is the mass concentration expressed in terms of the compound whose molecular weight was determined in 8.1.2.2.

8.2 Organic Solvent Concentration

8.2.1 Solvent Standards Concentrations. Calculate each solvent standard concentration prepared in accordance with Section 7.2.1.2 as follows:

$$C_c = \frac{B(d.\ \frac{mg}{\mu l})\ \frac{10^3\ \mu g}{mg}}{V_m\ Y\ \frac{293}{T_m}\ \frac{P_m}{760}} \qquad \text{Equation 1}$$

where:

C_c = Solvent standard concentration, µg/l.

B = Number of µl of solvent injected.

V_m = Gas volume measured by dry gas meter in liters.

Y = Dry gas meter, calibration factor.

P_m = Absolute pressure of the dry gas meter, mm Hg.

T_m = Absolute temperature of the dry gas meter, °A.

d. = Density of the solvent at 293°A.

8.2.2 Solvent Emission Concentrations The emission values in µg/ml are taken from the solvent standards response curve. No further calculations are required.

9. References

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